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Tungstic Acid for Preconcentration and Determination of Gaseous and Particulate Ammonia and Nitric Acid in Ambient Air

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16. ABSTRACT

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JOURNAL ARTICLE

Tungstic Acid for Preconcentration and Determination of Gaseous and Particulate Ammonia and Nitric Acid in Ambient Air

Robert S. Braman* and Timothy J. Shelley

Department of Chemistry, University of South Florida, Tampa, Florida 33620

William A. McClenny

Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

Tungstic acid surfaces chemisorb NH_3 and HNO_3. Collection of these gases is possible by sampling with a hollow tube, the interior of which is coated with tungstic acid. Under conditions of laminar flow, the gases diffuse to the wall and are chemisorbed while particles are carried through the tube. Particles are collected with an in-line tube packed with tungstic acid coated sand. Thermal desorption followed by a simple separation and detection by a chemiluminescent NO_x analyzer permits analyses at the parts per billion and lower concentration range for gaseous and particulate forms of the analytes. Detection limits are 1–3 ng/sample. The precision of analyses of ambient air samples is in the 5–10% relative standard deviation range. Coated hollow tubes conform sufficiently to the mathematical model of tube gas dynamics so as to permit reasonable determination of gaseous diffusion coefficients at ambient concentrations.

Ammonia, nitric acid, and sulfuric acid aerosol are important factors influencing the acidity of air and acidity of rain. Ammonium nitrate and ammonium sulfate are solid compounds resulting from atmospheric acid–base reactions of the three acid rain components. Thus, both gaseous and particulate forms of ammonia and nitric acid are expected to be present in air.

The determination of gaseous ammonia and nitric acid at the trace concentrations (0.1–5.0 $\mu g/m^3$) present in comparatively nonpolluted, ambient air as well as discrimination of gaseous from particulate forms is a difficult task. A number of workers have noted particle to gas or gas to particle conversion reactions on filters used to separate particles from the gas phase. A discussion of this aspect of previous work is given in our companion article (*1*).

Analytical procedures for gaseous ammonia have involved absorption on an oxalic acid treated surface as in the ring oven technique of Shendrikar and Lodge (*2*) modified by Cattell and DuCross (*3*). Gillett and Ayers (*4*) report the detection limit of this method to be near 0.05 μg/sample in routine use. Ferm (*5*) has used an oxalic acid coated diffusion tube to collect NH_3 later determined by ion-selective electrode. McClenny and Bennett (*6*) have reported a method for gaseous ammonia based upon absorption on Teflon beads after filtration to remove particulate ammonia. Collected gaseous ammonia was desorbed by heating and detected by using a photoacoustic detector. The detection limit was approximately 5 ng/sample.

Gaseous nitric acid has been collected on sodium chloride impregnated filters after removal of particles by a nontreated prefilter (*7, 8*). Total gaseous and particulate nitrates can be collected on filter combinations such as, for example, a quartz fiber filter and a nylon filter (*9*).

Shaw et al. (*10*) developed a method for nitric acid in air employing two parallel sampling lines, one of which includes a diffusion denuder tube to eliminate HNO_3. Both total and particulate HNO_3 are determined and the difference is gaseous HNO_3.

The work reported here started with a preliminary study of new approaches to the preconcentration and determination of gaseous ammonia in air. A variety of metal and metal oxide coated tubes were evaluated in preliminary work for ammonia retention and thermal desorption. Tungsten- and molybdenum-coated glass beads retained ammonia and released it upon heating. Tungsten functioned at lower temperatures and could also be more easily coated onto surfaces. Later work revealed that the active tungsten coating was a mixture of tungsten(IV) and -(VI) oxides in forms hydrated at least in part to tungstic acid. It was also found that, fortuitously, nitric acid was also retained on the tungstic acid coatings and released as NO_2. Thus, the simultaneous collection of both nitric acid and ammonia was possible.

The success of Ferm (*5*) in avoiding particle–gas reactions on filters and the previous successful applications of diffusion tubes by Stevens et al. (*11*) and Durham et al. (*12*) suggested the use of tungstic acid interior coated tubes. A method of successfully preparing such tubes was eventually developed. A combination, then, of tungstic acid coated hollow tube followed by a packed tube provided for preconcentration of both gaseous and particulate ammonia and nitrates. A commercial model Bendix NO_x analyzer was used as the detector to provide for the approximately 1 ng detection limit and the high specificity needed.

Evaluation of the breakthrough capacity and efficiency of the hollow tubes led to the modification of the equations which have been developed describing hollow tube operation. A section-by-section hollow tube analysis procedure was also developed which permitted calculation of the diffusion coefficients of gaseous ammonia and nitric acid in the environment at ambient concentrations.

EXPERIMENTAL SECTION

Tungstic Acid Tube Preparation. Tungsten(VI) oxide (which hydrates to tungstic acid) surfaces on silica sand and on hollow tubes were prepared by vacuum deposition from 0.020 in. diameter tungsten wire obtained from Research Organic/Inorganic Corp., Sun Valley, CA. White silica beach sand was prepared for coating by boiling with concentrated HCl to remove acid-soluble trace metals, water washing, drying, and sieving to 45–60 mesh. Coils of tungsten wire were attached to leads of 0.125 in. copper tubing sealed at the ends and suspended 2 cm above the sand in an evacuated glass chamber. A vacuum of approximately 1 torr was maintained. Approximately 10 g of dry sand was coated by passing a current of 6 A through the tungsten coil for 6 to 10, 15-s intervals. Cooling periods were allowed between coating intervals to avoid overheating an iron stirring bar used to stir the sand. A coating of polymeric blue tungsten oxide is produced

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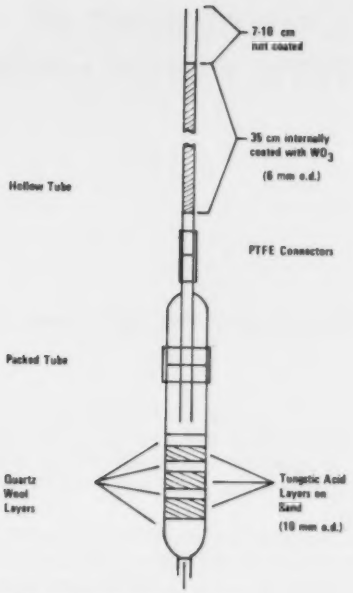
7-10 cm not coated
35 cm internally coated with WO_3 (6 mm o.d.)
Hollow Tube
PTFE Connectors
Packed Tube
Quartz Wool Layers
Tungstic Acid Layers on Sand (10 mm o.d.)

Figure 1. Hollow and packed tube designs.

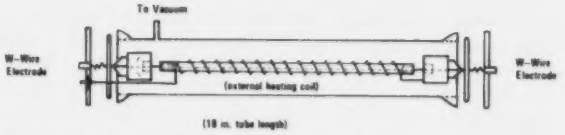

Figure 2. Apparatus for coating hollow tubes.

on the sand. Quartz tubes are packed with three sections of tungsten(VI) oxide coated sand (Figure 1) to avoid cracking when heated. The lead in glass tube is used to deposit the particulate directly on the quartz wool surface to avoid particle collection around the unheated part of the packed tubes and subsequent loss in analysis.

Hollow tubes are coated by using the vacuum deposition apparatus shown in Figure 2. The 6 mm o.d., 45 cm long quartz or Vycor tubes are prepared for coating by benzene washing, treatment with hot 50% NaOH, water washing, HF washing, and oven drying. Tungsten wire is suspended in the center of the quartz or Vycor tube by spring-loaded attachments on both ends. A vacuum of 0.5 torr or less is maintained during degassing and coating. An auxiliary wire coil heater is used to first degas the tube at dull red heat for 5 min. Following this, the 50 cm of tungsten wire is heated by passing through it an ac current of approximately 12 A for 30 min (light coating) to 2 h (heavy coating). The current is controlled by an autotransformer and must be adjusted so that a slow coating rate and a glassy oxide coating are obtained. Tubes can be rapidly coated at higher currents but a much more powdery surface results with less desirable desorption characteristics. Vycor appears to coat more easily and have a more mechanically stable coating than quartz. The end inserts provide for the uncoated parts of the hollow tube design.

Both the packed and hollow tubes contain polymeric blue tungsten oxide after completion of the coating process. The polymeric blue tubes produce high ammonia blanks while the oxidized tubes do not. Consequently, both tubes must be oxidized to the yellow (orange when hot) tungsten(VI) oxide prior to use in preconcentration and analysis. Packed tubes are heated to approximately 500 °C with the same heater coil used in analysis while passing oxygen through the tube. Excessive heating causes migration of the oxide and uncoated spots on the tube, a feature useful when removing WO_3 from the tube ends. All tubes were conditioned prior to use. Standard samples of 50–200 ng of NH_3 were added to and analyzed on a tube until response became reproducible. This usually required four to six analyses initially. Sample responses were low at first, an effect which is attributed

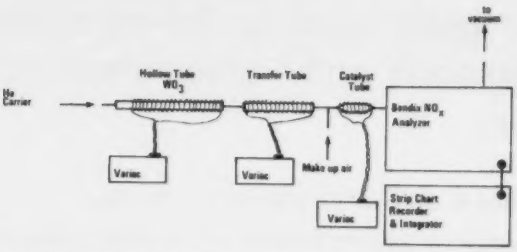

Figure 3. Apparatus for preconcentration tube analysis.

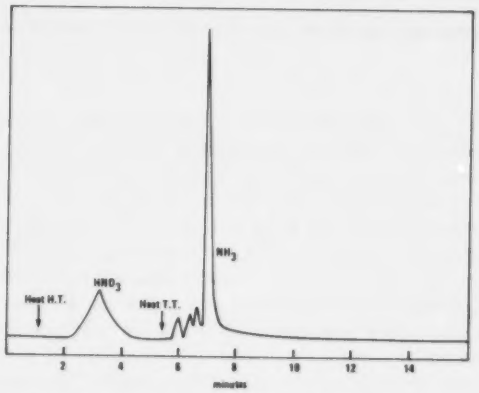

Figure 4. Analysis response for HNO_3 and NH_3.

to partial penetration of the WO_3 by NH_3 and absorption on less available acidic sites. Conditioning of tubes using nitric acid gives a similar result. Maintenance of proper conditioning should be checked by running standards periodically. In an automated version of this method, tubes were found to retain conditioning for 2–3 weeks of continual cyclic use. Nevertheless, it is recommended that conditioning be checked using standards after 10 samples.

Apparatus Arrangement. The analysis apparatus developed is shown in Figure 3. It consists of a preconcentration tube heater, a transfer tube and heater, and a Bendix NO_x analyzer. Helium carrier gas is used to carry desorbed gases through the system. A gold catalyst bed is used to convert ammonia to NO. The NO_x analyzer functions at a reduced pressure with an inlet flow rate of approximately 150 mL/min. The carrier gas flow rate is approximately 75 mL/min. The makeup air is needed to oxidize ammonia in the carrier gas from the preconcentration tube system.

Several different designs of the gold catalyst bed were used during studies. Either gold-coated coarse silica sand or pieces of gold metal serve to quantitatively oxidize ammonia. The catalyst bed is heated above 600 °C by means of a coiled heater wire. The present design with gold strips has the advantage of a low pressure drop.

The transfer tube, which also has a tungstic acid coating, is used to improve the separation of nitric acid response from ammonia response as described later. An integrating strip chart recorder, Model No. 252A, Linear Instrument Co., was used in recording and processing response data.

Analysis Procedure. In the tube analysis procedure the preconcentration tube is heated to approximately 350 °C while the transfer tube is maintained slightly warm. Nitric acid is converted to NO_2 and is not absorbed by the transfer tube. Nitric acid is detected immediately. Ammonia released at the same time in the heating of the preconcentration tube is absorbed onto the transfer tube. After the nitric acid signal has decreased to a base line, the transfer tube is heated to drive off the absorbed ammonia. Thus, the separation between nitric acid and ammonia signals can be made as great as desired. A typical analysis is shown in Figure 4. All four of the ammonia peak areas are used in calculating response.

Calibration. Calibration of instrument response and the generation of standard samples in air were done chiefly by the use of a permeation tube for NH_3 and a diffusion tube system

for HNO_3 (*13*). Permeation rates of NH_3 and diffusion rates of HNO_3 were determined gravimetrically. Both standards were prepared so that low parts per billion concentrations of NH_3 and HNO_3 could be prepared in a single dilution step in a mixing chamber. Compressed breathing air having low humidity and low oil content was used as the air diluent. This was found superior to compressed air from the laboratory building system which had some oil and both NH_3 and HNO_3 present. The compressed breathing air contained no NH_3 or HNO_3. With this mixing system it was possible, by knowing the sampling flow rate, carrier gas rate, and permeation or diffusion rate, to calculate the amount of NH_3 or HNO_3 standard on the tungstic acid tubes. Response curves were prepared in units of ng NH_3 or HNO_3 vs. relative area response. Sample sizes found in environmental analyses were generally in the 0–100 ng range, and consequently calibration curves were prepared over this range. Calibration curves were linear for both NH_3 and HNO_3. Hollow tubes do not have to be individually calibrated as all give an equivalent response for the same compound.

Solutions of $(NH_4)_2SO_4$, NH_4NO_3, and $NaNO_3$ were used as well as the gases for calibration of response in some experiments. Solutions of the pure compounds were prepared and an appropriate dilution made so that 10–100 μL of solution could be used to deliver 10–100 ng of standards. The solutions were injected onto packed tubes which were allowed to dry slowly at room temperature while passing a stream of carrier gas through the tube. Nitrate salts gave responses typical of and equivalent to nitric acid. Ammonium salts gave a response equivalent to ammonia. Ammonium nitrate gave a response for both HNO_3 and NH_3. Packed tubes also all give the same response for the same compound and do not have to be individually calibrated. This method of solution analysis can also be used for analysis of freshwater and rain water. If 50-μL samples are used for analysis, the detection limit is approximately 0.02 ppm for nitrates (plus nitrites) and ammonium ion in water. The procedure has the advantage that both can be determined on the same sample in the same analysis.

Detection Limits and Precision. Detection limits under the best of conditions are on the order of 1–3 ng/sample depending upon the compound detected and calculated from the precision in response of 5–10 ng samples. Since ammonia and nitric acid give the same response in the NO_x analyzer on a molar basis, ammonia has the lower weight detection limit. Concentration detection limits are generally in the 0.01 ppb range for 20-L samples. Both hollow and packed tubes have the same detection limits.

The precision of analyses was determined in one study of duplicate results using packed tubes. For 19 pairs of tubes having an average of 50 ng of HNO_3 present, the mean difference between pairs was 5.3% RSD. For 18 pairs of tubes having an average of 6 ng of NH_3 present, the mean difference between pairs was 8.2% RSD.

Storage Blanks. Tubes well oxidized and conditioned for use do develop small NH_3 blank signals after several hours. One day blanks on both hollow and packed tubes for HNO_3 were found to be less than the detection limit. For ammonia they were on the order of 2–3 ng. Five day blanks for HNO_3 on hollow tubes were found to be less than the detection limit. On packed tubes the HNO_3 blanks were approximately 2 ng. Five day blanks for ammonia were 6–8 ng for both types of tubes. Some blank development may be due to diffusion of NH_3 and HNO_3 through the Parafilm seals used. Glass plug seals with PTFE Teflon connectors are an improvement but NH_3 blanks still develop slowly over several days.

Environmental Analysis Procedure. Air samples were drawn through the hollow tube–packed tube combination by means of a small diaphragm pump using a calibrated, valve-controlled rotameter. A mass flow meter has also been used to monitor flow rate. Sample flow rates used were generally in the 1–2 L/min range to accommodate the requirements of eq 1 for sampling efficiency. Up to 30-min samples were generally taken except on a few occasions when 1 to 2 h of sampling were needed to preconcentrate from very low concentrations of ambient samples. Sampling tubes were mounted vertically to avoid gravity deposition of particles. Preconcentrated samples were generally analyzed within 2 h of collection to avoid buildup of ammonia blanks. Tubes stored prior to analysis were sealed with Parafilm.

RESULTS AND DISCUSSION

Absorption and Desorption Chemistry. The chemistry of absorption and desorption of ammonia on the tungsten oxide tubes is not entirely clear, partly because of the complexity of composition of tungsten oxides. Initial work was done with the blue tungsten oxide. The blue oxide was formerly considered to be W_4O_{11}, an oxide in which one in each of four tungsten atoms is in the 4+ oxidation state. More recently, this has been shown to be a mixture of $W_{18}O_{49}$ and $W_{20}O_{58}$ (*14*). The oxidation of these produces the yellow oxide, WO_3, which can hydrate to H_2WO_4 or $H_2W_2O_7$. Tungstic acid is a weak acid and may be present in several forms involving the polymeric anions $W_6O_{21}^{6-}$, $HW_6O_{21}^{5-}$, $W_{12}O_{41}^{10-}$, and $H_2W_2O_7$ in addition to H_2WO_4. Formation constants reported for four acid species indicate a surface pH of approximately 3–4 (*15*, *16*). Thus, the absorption of ammonia is likely by an acid–base reaction

$$NH_3 + H_2WO_4 \rightleftarrows NH_4HWO_4$$

which is reversed by heating to approximately 350 °C. The four peaks noted in the thermal absorption of ammonia, as seen in Figure 4, are likely due to the decomposition of four different ammonium tungstates occurring at slightly different temperatures as the tube is heated. The first three peaks in the desorption are of approximately the same area each and together account for approximately 20% of the total ammonia absorbed. The more thermally stable ammonium tungstate detected as the last peak is likely the ammonia compound formed with the strongest tungstic acid.

Tungsten(VI) oxide is reported to undergo a crystal structure change from monoclinic to orthorhombic at 320 °C. A color change from yellow to yellow-orange is apparently associated with this and serves as a convenient temperature indicator—when heating the preconcentration tubes for analysis.

The mechanism of nitric acid absorption is not clearly understood but experimental work indicates that irreversible chemsorption is involved. Absorption may take place due to formation of the inorganic acyl nitrate.

$$WO_2(OH)_2 + 2HNO_3 \rightarrow WO_2(NO_3)_2 + 2H_2O$$

or

$$WO_2(OH)_2 + HNO_3 \rightarrow WO_2(OH)(NO_3) + H_2O$$

The compound $WO_2(NO_3)_2$ has been prepared by reaction of N_2O_5 with WO_3 (*17*). The absorption of nitric acid could also be considered to be formation of a heteropoly acid with tungstic acid. Thermal decomposition of this type of compound would then occur in a manner similar to that of other nitrates.

$$WO_2(NO_3)_2 \rightarrow {}^1/_2O_2 + 2NO_2 + WO_3$$

Thermal decomposition of nitrates appears to occur at temperatures just below the temperature needed for ammonia release from the tungstic acid tubes. Generally, only a single broad peak is observed in nitric acid desorption.

Mathematical Model for Tubes of Finite Capacity. Ferm (*5*) detailed the mathematical function of hollow tube operation in describing the oxalic acid tube method for ammonia. This is in part valid for the present application but has been extended by us to provide for tube depletion, present when tubes have a finite capacity. Gormley and Kennedy (*18*) were the first to derive the accurate equations for describing mass transfer from an air stream to the walls of a hollow tube. Assumptions are made that air flow is laminar, i.e., the velocity distribution of the air stream is parabolic and that wall collisions are inelastic. Molecular collisions with the wall must

result in chemisorption. Establishment of laminar flow requires a nonabsorbing section of tube length

$$L = 0.1r\ \mathrm{Re}$$

where r is the tube radius and Re is the Reynolds number. For tubes having inside diametrers of 0.3–0.4 cm and air flow rates in the 0.5–2.0 L/min range, Re is less than 100. Consequently, a nonabsorbing section of a 0.4 cm diameter tube 5–10 cm long will be more than sufficient to develop laminar flow.

The Gormley–Kennedy equation (*18*), eq 1 given below, is

$$C/C^\circ = 0.819\ \exp(-3.6568\Pi DLF^{-1}) + 0.0976\ \exp(-22.3\Pi DLF^{-1}) + 0.032\ \exp(-57\Pi DLF^{-1}) \quad (1)$$

the first three terms of a series solution to a differential equation, where C/C° is the fraction of molecules that penetrate the active section of a hollow tube under experimental conditions of D diffusion coefficient, tube length L, and sample flow rate F. For the grouping $\mu = \Pi DLF^{-1}$, where $\mu = 0.10$ and larger, only the first term of eq 1 is significant. For example, at $\mu = 0.10$, $C/C^\circ = 0.58$ with less than 2% contribution from the second term. For ammonia and the sampling tubes and flow rates used in analyses reported here, $\mu = 1.6$ and the second term of eq 1 is on the order of 1×10^{-13} the value of the first term.

Equation 1 was used by Fuchs (*19*), Davies (*20*), and Ferm (*5*) to describe an absorption tube of infinite capacity. This may be a reasonable model for the impact collection of particles, but it is not when a rapid, irreversible chemisorption on a tube having a finite number of sites is involved. If a tube has a finite capacity the effective length of the tube, L in eq 1, changes with sampling time. Tube depletion depends upon sample concentration and the concentration of absorption sites per unit area. Consideration of the physical model indicates that the effective length changes exponentially with time because efficiency changes exponentially with length. Thus, the effective length, L, at time, t, is related to the original effective length L_o by

$$L = L_o \exp(-kt) \quad (2)$$

where k is the tube depletion rate constant. The depletion rate constant is related to the analyte feed rate and total tube capacity in nanograms of analyte.

$$k = \frac{\text{feed rate (ng/min)}}{\text{tube capacity (ng)}}$$

Equation 1 combined with eq 2 and using only its first term gives

$$C/C^\circ = 0.819\ \exp[-3.6568\Pi DF^{-1}L_o\ \exp(-kt)] \quad (3)$$

As will be demonstrated, eq 1 and 3 are useful for predicting the efficiency of tubes in operation. Equation 3 is useful for analyzing tube breakthrough capacity experiments, a fact which also demonstrates its validity.

When μ becomes smaller than 0.10 as is the case for particles or molecules having small diffusion coefficients, eq 1 becomes increasingly inaccurate and the following must be used

$$N/N^\circ = 1 - 2.56\mu^{2/3} + 1.2\mu + 0.177\mu^{4/3} \quad (4)$$

where N/N° is the fraction of particles passing through the tube. For particles of 0.1 μm size and larger under sampling conditions used here $N/N^\circ = 0.999$ or larger. Thus, diffusional collection of particles is theoretically small. As Ferm (*5*) has demonstrated, the collection of large particles by gravitation is small and avoidable if tubes are mounted vertically.

Since eq 1 contains a gaseous diffusion coefficient for the analyte gas, the hollow tube collection technique can be used to obtain diffusion coefficient values if experimental conditions are carefully controlled. Two examples of this are section by section analysis of tubes and diffusion coefficients from tube efficiency data, the mathematical treatments of which follow.

Section by Section Analysis Model. Chemisorbed compounds should be distributed, according to eq 1, along a hollow tube as a function of their diffusion coefficient in air. Compounds having comparatively large diffusion coefficients are more concentrated near the entering end of the tube. Compounds having smaller diffusion coefficients will be more distributed along the tubes. A section by section analysis of a sampled hollow tube, therefore, should provide at least a qualitative indication of the type of compound or compounds adsorbed.

Data from the section by section analysis technique can theoretically be used to determine the mean diffusion coefficient of absorbed NH_3 and HNO_3 or compounds giving comparable responses. This can be shown by a mathematical treatment of the multisection model of hollow tubes. In this model it is assumed that tubes are uniform in character and that tube depletion is minimal in any section, a condition approached in most cases except for high-analyte concentrations.

The amount of a compound found in each section is dependent upon absorption efficiency, analyte concentration, gas, flow rate, F, and sample volume, V. For the first three sections one can write

$$S_1 = (C^\circ - C_1)V \quad (5)$$

$$S_1 = C^\circ(1 - C_1/C^\circ)V \quad (6)$$

$$S_2 = C_1(1 - C_2/C_1)V \quad (7)$$

$$S_3 = C_2(1 - C_3/C_2)V \quad (8)$$

From eq 1

$$C_1/C^\circ = 0.819Q_1 \quad (8)$$

where Q_1 is the exponential term for length, L, of section 1. Similarly, for sections 2 and 3

$$C_2/C^\circ = 0.819Q_{1+2} \quad (9)$$

$$C_3/C^\circ = 0.819\ Q_{1+2+3} \quad (10)$$

where Q_{1+2} and Q_{1+2+3} are for terms for lengths $L + 2$ and $L + 2 + 3$, respectively. From this, if all sections are equivalent in length, then $Q_1 = Q_2 = Q_3$, etc. and

$$C_2/C_1 = Q \quad (11)$$

$$C_3/C_2 = Q \quad (12)$$

then

$$S_2/S_1 = C_1/C^\circ\ \frac{(1 - Q)}{(1 - 0.819Q)} \quad (13)$$

and

$$S_3/S_2 = C_2/C_1 \quad (14)$$

by analogy

$$S_n/S_{n-1} = C_{n-1}/C_{n-2} \quad (15)$$

For tubes 30 cm long S_2/S_1 approaches C_1/C° in value. Otherwise, in using S_2/S_1 it is necessary to assume approximate values of the diffusion coefficient involved and then to obtain improved values from successive estimates of C_1/C°. If sections are not of equivalent length, albegraic forms of S_n/S_{n+1} retaining Q values for each section can be developed and used in evaluating experimental data.

Preconcentration Efficiency. Preconcentration efficiency is related to the section-by-section treatment in that longer sections are used. Efficiency for section 1 is defined as S_1/S_T where S_T is the total analyte compound passed through the tube. Reasonably good values of S_T are determined experimentally by using two long tubes attached in

Table I. Adsorption Efficiency

compd	efficiency, % found	efficiency, % calcd	flow rate, L/min
	Hollow Tubes		
HNO_3	89.0	89.0	1.4
HNO_3	95.0	95.1	1.0
HNO_3	94.3	95.1	1.0
HNO_3	96.9	95.1	1.0
NH_3	98.6	99.7	0.86
NH_3	95.6	99.7	0.96
$(CH_3)_2NH$	99.0		0.96
	Packed Tubes (Two-Section)		
$NH_3(g)$	84-90 (N = 6)		1
	Packed Tubes (Three-Section)		
$NH_3(g)$	96-99+ (N = 4)		1
$NH_4^+(s)$	75-78 (N = 4)		1
$NO_3^-(s)$	76-86 (N = 4)		1
L = 34 cm	$D(HNO_3)$ 0.12	$D(NH_3)$ 0.236	

tandem whereby $S_1 + S_2$ is essentially S_T. Efficiency is related to C/C° and Q_1 as follows using eq 1 and 5.

$$S_1/S_T = \frac{C^\circ(1 - 0.819Q_1)V}{C^\circ V} \tag{16}$$

Consequently

$$S_1/S_T = 1 - 0.819Q_1 \tag{17}$$

which also can be used to calculate diffusion coefficients. This approach was found to have the advantage of providing the best precision for diffusion coefficient determinations since the impact of the tube depletion is minimal and the precision of S_1 and S_T is better than that of S_1, S_2, etc.

Absorption Efficiencies. The efficiency for gas absorption by hollow tubes depends upon the flow rate and tube length in accordance with eq 1. Table I gives data on the absorption efficiency determined in several tests with standard air samples. The amounts of analyte used were 10–20% of the tube capacity. Generally, the tubes were found to have efficiencies equivalent to those calculated from theory. Similar efficiencies have been noted using the same tubes in occasional tests with outdoor air and over a range of relative humidities from 55 to 85%.

Three-section packed tubes have efficiencies for gases on the same order as the hollow tubes and have a capacity of 1–2 μg. Nevertheless, particulate penetration of the packed tubes is approximately 22%, as determined by analysis of outdoor air after removal of gaseous HNO_3 and HN_3. The efficiency values are reasonably constant for a tube and may be used in corrections of particulate data. Larger packed tubes can be used to improve efficiency but this lowers sample flow rates attainable.

Particulate efficiency may vary somewhat dependent upon the particle size distribution encountered. Products from gaseous decompositon of the particulate will be effectively reabsorbed by the tungstic acid coating on the sand.

Breakthrough Capacity Studies. Breakthrough capacity studies were done both on the tungstic acid hollow tubes described here and on oxalic acid coated tubes. The oxalic acid tube method of Ferm (5) was being studied at the same time. Since the total ammonia capacity of oxalic acid coated tubes was greater than that of the tungstic acid tubes, an NH_3 permeation tube having a higher permeation rate was used for the oxalic acid tube experiments. A diffusion type generation system was used in experiments with HNO_3. The HNO_3 and NH_3 in air generation systems were placed in series with the hollow tubes and the NO_x detector. The NO_x analyzer and strip chart recorder were used to continuously record NH_3 or HNO_3 passing through the tubes.

Table II. Breakthrough Data for Hollow Tubes

L_o(apparent), cm	L(measd), cm	F, mL/min
Tungstic Acid Tubes-NH_3		
1. $\ln(-\ln C/C^\circ(0.819)) = -0.1017 \pm 0.0011\ min^{-1} + 2.171 \pm 0.018$		
31	25	580
capacity at $C/C^\circ = 0.10$; 840 ng of NH_3		
2. $\ln(-\ln C/C^\circ(0.819)) = -0.1149\ min^{-1} + 2.623r = 0.995$		
83	33	980
capacity at $C/C^\circ = 0.10$; 890 ng of NH_3		
3. $\ln(-\ln C/C^\circ(0.819)) = -0.747\ min^{-1} + 2.714r = 0.997$		
114	33	1.23
capacity at $C/C^\circ = 0.10$; 160 ng of NH_3		
Tungstic Acid Tubes-HNO_3		
4. $\ln(-\ln C/C^\circ(0.819)) = -0.4404\ min^{-1} + 1.9674r = 0.999$		
71	34	1.03
capacity at $C/C^\circ = 0.10$; 625 ng of HNO_3		
5. $\ln(-\ln C/C^\circ(0.819)) = 0.2841\ min^{-1} + 1.2397r = 0.998$		
34.3	34	1.03
capacity at $C/C^\circ = 0.10$; 620 ng of HNO_3		
Glycerol-$H_2C_2O_4$ Tube		
6. $\ln(-\ln C/C^\circ(0.819)) = -0.462\ h^{-1} + 1.902\ 4 = 0.999$		
38	35	0.943
capacity at $C/C^\circ = 0.10$; 54 μg of NH_3		

Typical sigmoidal type breakthrough curves were obtained. Several of the oxalic acid tubes prepared by evaporation from methanol, according to the reported method (5), gave poor absorption efficiencies from the start. This was attributed to a poor surface coverage by oxalic acid and was remedied by adding 0.50 mL of glycerol to the 10 mL of methanol–1% oxalic acid solution used in the tube coating. Glycerol leaves a much better coating on the tube interiors.

Tube capacities and depletion rate data calculated from eq 3 are given in Table II. A plot of ln [$-\ln C/C^\circ(0.819)$] vs. t for a tungstic acid tube is shown in Figure 5. A plot of ln $C/C^\circ(0.819)$ vs. t is also shown, demonstrating, as predicted, that C/C° is not constant with time as the effective length changes. The plot of eq 3 demonstrates its validity. Nevertheless, as can be seen from data in Table II tubes 3 and 4, the calculate L_o value using the experimental data is not always the real physical length of the coated hollow tubes. This may be due to a slow penetration rate of ammonia into the tungstic acid layer during the breakthrough run giving the apparent greater length. The differences in depletion rates are attributable to different feed rates and different compounds used in the experiments.

Tubes tested in 1 and 2 were of comparatively high surface area. If coating is done rapidly in the presence of a high oxygen partial pressure or at a higher temperature, the surface is less smooth. Consequently, a larger number of reactive sites are available and a larger capacity is observed. Tubes used in 3, 4, and 5 were prepared by a slow coating at a lower vacuum pressure and the coating was smoother and more glasslike. These had a lower capacity.

A comparision of breakthrough capacity of the same tube for HNO_3 vs. NH_3 was made and run in duplicate. The NH_3 capacity of one tube at $C/C^\circ = 0.10$ was 160–190 ng. The HNO_3 capacity of the same tube at $C/C^\circ = 0.10$ was 625–620 ng. On a molar basis the capacities of the two tubes are

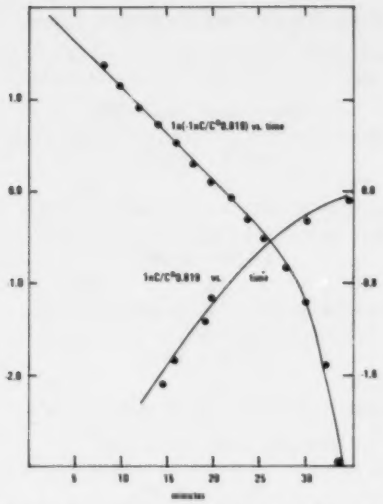

Figure 5. Plots of breakthrough capacity curve data: (upper curve) left scale; (lower curve) right scale.

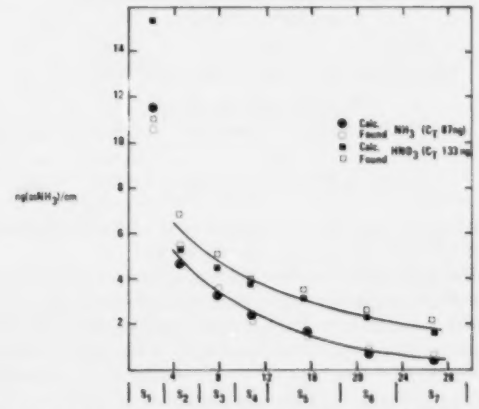

Figure 6. Section by section analysis for environmental HNO_3 and NH_3.

essentially the same indicating that the active site on the tungstic acid surface is capable of absorbing either NH_3 or HNO_3.

Section by Section Analyses. In order to perform this type of analysis a special tube heater was constructed having 12 individually heated sections of approximately 3 cm length each. This heater mounted with the tube to be analyzed was placed in the analysis apparatus in front of the transfer tube. Sections were heated and analyzed sequentially starting with the sample exit end of the tube first. All sections analyzed were kept heated to the desorption temperature. Section 1 was analyzed first by heating it alone. Sections 1 and 2 were then both heated to give an analysis of section 2. The rest of the tube was analyzed in the same manner. Although the 12 section analysis approach gave a good qualitative picture of how an analyte was distributed down the tube, it was found that longer sections gave better accuracy in determining diffusion coefficients.

Analyses of ammonia and nitric acid standards and of various ambient air samples were made with results conforming to the expected. Figure 6 gives a typical section-by-section analysis for an air sample taken in the Eastern Gulf of Mexico showing the distribution for both nitric acid and ammonia. The smaller diffusion coefficient for HNO_3 results in its being more distributed down the tube. Results of environmental analyses generally show agreement of environmental NH_3 and HNO_3 with laboratory standards. A non-

Table III. Diffusion Coefficients from Tube Analysis

D, cm^2/s	F, cm^3/s	L, cm	temp, °C
	NH_3 (permeation standard)		
	$\bar{X}$ 0.236 cm^2/s		
0.239	46.33	33.0	26
0.194	15.87	11.3	23
0.253	15.87	11.3	23
0.257	27.83	17.0	23
	HNO_3 (diffusion standard)		
	$\bar{X}$ 0.121 cm^2/s		
0.125	16.15	32.5	24
0.123	16.00	32.8	24
0.114	16.10	33.5	23
0.128	16.84	33.1	21
0.117	16.77	34	26

typical distribution of compounds down the length of the tube has been observed in some environmental samples analyzed. This was attributed to the presence of higher molecular weight peroxyacylnitrate (PAN) compounds or organic amines in addition to NH_3 and HNO_3.

Diffusion Coefficient Determinations. Diffusion coefficients have been determined for NH_3 and HNO_3 using the section analysis approach. The best results appear to be obtained using a pair of long hollow tubes and eq 17. Data from several experiments are given in Table III. Nitric acid diffusion coefficients approximate the 0.122 cm^2/s value calculated by the method of Wilke and Lee (*21*). The NH_3 diffusion coefficients agree with the 0.236 cm^2/s value reported (*21*). Use of the tungstic acid method for more accurate determinations of diffusion coefficients required tubes well conditioned with standards and particular care not to overheat any section.

It is apparent, of course, that the best values for diffusion coefficients from the use of eq 17 require accurate analyses of analytes trapped on each section and a minimal tube depletion. This is generally achieved at higher carrier gas flow rates and lower total samples sizes. A more thorough study of this hollow tube method for accurate determination of diffusion coefficients is indicated. The present degree of agreement between theoretical and experimental data is reasonable.

The diffusion coefficient values obtained in environmental analyses indicate that NH_3 is in a monomolecular, nonassociated form. Nitric acid may be associated with water or some other compound thus decreasing their apparent diffusion coefficient. In one circumstance, for example, HN_3 and HNO_3 had apparent diffusion coefficients of 0.08 and 0.05 cm^2/s, respectively. This sample had been taken in the proximity of a grass fire. Presumably the nitrogen compounds or molecular associations were responsible for low observed diffusion coefficients.

Interferences and Limitations. Mono-, di-, and trimethylamine are retained on the tungstic acid surfaces in a manner similar to ammonia. The amino–tungstates decompose at approximately the same temperature and the released amines are oxidized in the catalyst bed to NO. Consequently, it appears as if all alkylamines having any base character will be interferences.

Nitrogen dioxide was considered a potential interferant in the nitric acid part of the method. Consequently, a careful study was carried out to determine the effect of NO_2 on tube response. A dynamic gas double dilution system was assembled consisting of a NO_2 permeation tube, a humidifier section for the compressed air, and a tube packed with granular NaCl. The NaCl packed tube placed downstream of the NO_2 permeation tube was needed to remove HNO_3 from the feed NO_2

Table IV. Nitrogen Dioxide Interference Studies[c]

RH,[a] %	NO_2 feed,[b] nm	amt found, nm (%)		samples	
		HNO_3	NH_3	min	liters
84	11.0	0.083 (0.8)	0.21 (1.9)	10	7.2
84	11.0	0.051 (0.5)	0.22 (1.9)	10	7.2
80	50.0	0.22 (0.4)		50	36
80	50.0	0.20 (0.4)		50	36
74	33.5	0.06 (0.2)	0.26 (0.8)	60	43
74	43.4	0.39 (0.9)	1.21 (2.7)	70	50
70	5.77	0.05 (0.9)	0.1 (1.7)	10	13.6
70	5.77	0.05 (0.9)	tr	10	13.6
24	5.77	0.08 (1.4)	tr	10	13.6
24	5.77	0.05 (0.8)	0.37 (2.9)	10	13.6

[a] Relative humidity. [b] Nanomoles. [c] LineAir blanks: NH_3, 0.10 nm/10 min; HNO_3, 0.05 nm/10 min.

stream. Tests for NO_2 interference in HNO_3 analyses are difficult because NO_2 reacts slowly on surfaces with water to produce HNO_2 and HNO_3. Results on NO_2 interference tests are given in Table IV. The NO_2 exposure was determined by a colorimetric procedure (22). Line blank values for HNO_3 were not subtracted from HNO_3 found. Nitrogen dioxide is essentially no interference in either the HNO_3 or NH_3 analyses. The small signals observed are at least partly line blank amounts or can be attributed to some reaction of NO_2 and water on tube surfaces during the test period.

Ozone was tested for interference in ammonia analysis. Ozone at approximately 100 ppb appeared to decrease ammonia absorbed on the tungstic acid tubes by 5–10%.

Peroxyacetylnitrate (PAN) is a potential interferant in the HNO_3 method. A small amount of PAN was prepared in hexane according to the procedure of Kravetz, Martin, and Mendenhall (23). PAN vapor samples in the 50–500 mg range were not absorbed by the tungsten hollow tubes. Responses were less than the detection limits. PAN-type compounds of higher molecular weight presumably could physically sorb to an extent if collected and respond as HNO_3 in the analyzer.

A number of common volatile organic compounds were tested for interference by sampling air containing their vapors. No responses were obtained for milligram amounts of ethanol, benzene, chloroform, carbon tetrachloride, methylene chloride, formaldehyde, xylene, and butane. In addition, hydrogen cyanide, sulfur dioxide, hydrogen sulfide, dimethyl sulfide, and nitric oxide do not interfere. These compounds are either not absorbed despite the fact that they do collide with the sampling tube walls or they are not detected by the detector. Particulate organic matter in the microgram to milligrams sample size collected on the packed tubes decomposes during the analysis step and can give a broad peak detected by the NO_x analyzer. The detector response is attributed to CO luminescence not completely filtered out by the optical system. Large amounts of retained organic matter can decompose during analysis leaving carbon and other residues in the sampling tubes. These must be removed by heating the tubes in the presence of oxygen to avoid lowered responses. Tubes cleaned in this manner need reconditioning by analysis of an NH_3 standard. In ordinary circumstances of air analysis tubes can be used for 10–15 analyses without collecting organic matter sufficient to lower responses.

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